8. (Thrice Amended) A method for forming a semiconductor device having a laminated structure of a dielectric made from a metal oxide and a CVD high melting point metal nitride film formed thereover, wherein said metal nitride film is directly formed on said dielectric film by introducing a source gas containing said high melting point metal into a chamber in which said [substrate] dielectric film is contained, said method comprising;

heating a substrate onto which said dielectric film is formed to a prescribed temperature in an ambient having a NH_3 atmosphere of no greater partial pressure than 1.0 Torr and no less than 0.1 Torr before the introduction of said source gas containing said high melting point metal.

REMARKS

This paper is being provided in response to the April 12, 2002 Final Office Action for the above-referenced application. In this response, applicant has amended claims 1 and 8 in order to more particularly point out and distinctly claim that which applicant deems to be the invention. Applicant respectfully submits that the amendments to the claims are all supported by the originally filed application, specifically at least at page 19.

The rejection of claims 1-11 and 13-36 under 35 U.S.C. §103(a) as being obvious over newly cited reference of DeBoer et al. (U.S. Patent No. 6,146,959, hereinafter referred to as "DeBoer") or newly cited reference of Huang et al. (U.S. Patent No. 6,057,189, hereinafter referred to as "Huang") in view of Tamaru or Nishikawa or Lee, is hereby traversed and reconsideration thereof is respectfully requested. Applicant

respectfully submits that the claims, as amended herein, are patentable over the cited references, whether taken separately or in any combination.

Claim 1 recites a method for forming a semiconductor device having a laminated structure including a dielectric film made from a metal oxide formed on a surface of a heated substrate and a CVD high melting point metal nitride film, where the metal nitride film is directly formed on said dielectric film by introducing a source gas containing the high melting point metal into a chamber in which the substrate is contained, the method including a step of heating the substrate in an ambient that is non-reactive with respect to the metal oxide formed on the surface of the substrate in the chamber where the non-reactive ambient includes at least one of a gas non-reactive with respect to the metal oxide contained in the dielectric film and NH_3 gas, and introducing into the chamber a source gas for forming the CVD-TiN film and NH_3 gas, following the heating step, and further where a temperature of the substrate is set at a prescribed temperature, before the source gas containing the high melting point metal is introduced into the chamber.

Claims 2 through 7 depend from claim 1 and recite further patentable features over the base claim. Dependent claim 2 recites that the non-reactive ambient treating step has a flow stabilizing step. Dependent claim 3 recites that the non-reactive gas is introduced during the flow stabilizing step. Dependent claim 4 recites that the treating step heats the substrate and the flow stabilizing step is after the heating step. Dependent claim 5 recites that the NH_3 gas is introduced into the chamber during the heating step. Dependent claim 6 recites that the NH_3 gas has a NH_3 partial pressure of no greater than

1.0 Torr and no less than 0.1 Torr. Dependent claim 7 recites that the non-reactive gas and the NH_3 gas are introduced into the chamber during flow stabilizing step.

Claim 8 recites a method for forming a semiconductor device having a laminated structure of a dielectric made from a metal oxide and a CVD high melting point metal nitride film. The metal nitride film is directly formed on the dielectric film by a source gas containing the high melting point metal in a chamber in which the dielectric is contained. The method heats a substrate to a prescribed temperature in an ambient with an NH_3 atmosphere of no greater partial pressure than 1.0 Torr and no less than 0.1 Torr before the introduction of the source gas containing the high melting point metal.

Claims 9-10 depend from claim 8 and recite further patentable features over the base claim. Dependent claim 9 recites a step of heating the substrate to a prescribed temperature and maintaining the temperature in a non-reactive gas, which is neither oxidizing nor reducing with respect to the metal oxide, and while the gas flow is stabilized. Dependent claim 10 recites that the NH_3 gas is introduced during the second half of the CVD film growing step.

Claims 11 and 13-29 depend from claim 1 and recite further patentable features over the base claim. Dependent claim 11 recites a step that is performed before the CVD high melting point metal nitride film is formed, of heating the substrate (on which the dielectric film made from a metal oxide is formed) in the chamber while introducing the non-reactive gas. Then performing a step of forming the high melting point metal nitride

film on the dielectric film by introducing a gas mixture comprising the NH_3 gas and the non-reactive gas, the non-reactive gas being in a volume amount that is larger than the NH_3 gas, and the source gas amount having less volume than the NH_3 gas. Dependent claim 13, as amended herein, recites that the dielectric film is a tantalum oxide (Ta_2O_5) film. Dependent claim 14 recites that the substrate is heated to between approximately 400°C and 700°C before the source gas containing the high melting point metal is introduced. Dependent claim 15 recites that the non-reactive gas is selected from a list of nitrogen, argon, hydrogen gas, or a mixture of these gases. Dependent claim 16 recites that the high melting point metal nitride film is a TiN film. Dependent claim 17 recites that the source gas containing titanium is selected from the group consisting of titanium tetrachloride ($TiCl_4$), tetrakis dimethyl amino titanium (TDMAT), tetrakis diethyl amino titanium (TDEAT). Dependent claim 18 recites that the high melting point metal nitride film is alternately a WN film, and WF_6 gas is introduced as a source gas. Dependent claim 19 recites that the device has a capacitive element, a dielectric film, a CVD high melting point metal nitride film as a protective film between the dielectric film and the capacitive element. Dependent claim 20 recites that the device has a MOSFET where the CVD high melting point metal nitride layer is the lowermost layer of the laminated gate electrode layer. Dependent claim 21 recites raising the partial pressure of the NH_3 gas during a second half of forming the CVD film on the metal oxide, so that annealing is done by the NH_3 gas. Dependent claim 22 recites that the dielectric film is a tantalum oxide (Ta_2O_5) film. Dependent claim 23 recites that the substrate is heated between approximately 400°C and 700°C. Dependent claim 24 recites that the non-reactive gas is selected from nitrogen, argon, hydrogen gas, or a mixture of these gases. Dependent

claim 25 recites the high melting point metal nitride film is TiN. Dependent claim 26 recites the source gas containing titanium is selected from the group consisting of titanium tetrachloride ($TiCl_4$), tetrakis dimethyl amino titanium (TDMAT), tetrakis diethyl amino titanium (TDEAT). Dependent claim 27 recites that the high melting point metal nitride film is a WN film, and WF_6 gas is introduced as a source gas containing tungsten. Dependent claim 28 recites that the semiconductor device has a capacitive element, a dielectric film, and a CVD high melting point metal nitride film as a protective film between the dielectric film and capacitive element. Dependent claim 29 recites that the semiconductor device has a MOSFET with a gate insulation film and the CVD high melting point metal nitride layer is the lowermost layer of the laminated gate electrode layer formed on the gate insulation film.

Independent claim 30 recites a method for forming a CVD-TiN film, wherein a titanium nitride (TiN) film is formed on a dielectric film that includes an oxide material formed by a CVD film forming process within a CVD film forming device. The method includes heating a substrate with the dielectric film in the CVD film forming device in an atmosphere with a gas that is non-reactive with respect to the dielectric film, including the oxide. Then forming the titanium nitride (TiN) film on the dielectric film in the CVD film forming device.

Claims 31 to 36 depend from independent claim 30, and recited further patentable features over the base claim. Claim 31 recites that the dielectric film including said oxide material is a tantalum oxide (Ta_2O_5) film. Claim 32 recites that the substrate is heated to a

temperature of approximately 400°C to no greater than approximately 700°C. Claim 33 recites that the atmosphere including the non-reactive gas with the tantalum oxide comprises gases other than the NH_3 gas. Claim 34 recites that the atmosphere of non-reactive gas with the tantalum oxide comprises one gas selected from a rarified gas including nitrogen, argon, hydrogen gas, or a mixture of these gases. Claim 35 recites that the non-reactive gas is a mixture of titanium tetrachloride ($TiCl_4$) and NH_3. Claim 36 recites that the tantalum oxide film is formed as a capacitive film of a capacitor element and the CVD-TiN film is formed as a plate electrode.

The newly cited reference of DeBoer discloses a method of forming capacitors containing the metal tantalum. The disclosed method forms a dielectric layer having a dielectric constant of about 25 for a capacitor on a metal layer, typically hemispherical polycrystalline silicon. A silicon nitride layer 36 is deposited over the poly capacitor plate 34 in order to prevent the tantalum oxide layer from interacting negatively with the polysilicon layer 34. A first tantalum oxide layer 38 is formed over the nitride layer 36 and then a second tantalum layer 40 is formed by heating the first tantalum layer in an ambient containing nitrogen, such as ammonia. The tantalum layer 40 is thus tantalum nitride or tantalum oxynitride. Another metal nitride layer 42, such as titanium nitride or tungsten nitride, is formed over the second tantalum layer to provide protection for the tantalum oxide from the second polysilicon capacitor plate 44 (see col. 5, line 5).

The newly cited reference of Huang discloses a method of fabricating a capacitor using ion implantation to form a barrier layer of the outer part of the hemispherical poly

silicon capacitor plate. The polysilicon is ion implanted with nitrogen ions at 30 KeV to form a silicon nitride barrier layer to protect the future tantalum oxide dielectric from the polysilicon. The tantalum oxide is CVD deposited on the barrier layer, and then densified by annealing in oxygen or nitrogen (col. 4, line 54), to improve the electrical characteristics of the dielectric.

The cited art of Tamaru discloses a DRAM with a capacitive element that is protected from breakdown by a TiN film that is CVD deposited on the capacitor dielectric as a passivation film. The TiN film is to prevent the dielectric from making any contact with the nitrogen containing reducing gas (col. 3, lines 25 - 49).

The cited art of Nishikawa discloses a method of forming a dielectric film on a semiconductor substrate in a reduced pressure atmosphere, and then depositing a metal or metal nitride on the dielectric. Nishikawa discloses that hydrogen, carbon and methane released as a normal part of the CVD deposition causes electrical leakage in the dielectric film. Nishikawa discloses that this electrical leakage problem is reduced by using oxygen containing gases (which would be oxidizing with respect to the metal oxide) in the formation of the conductor film (col. 2, lines 18-27; col. 4, line 66; col. 9, line 15). Nishikawa states that this oxygen containing step is extremely important (col. 2, line 63), and thus Nishikawa does not teach using an inert ambient.

The cited art of Lee discloses a method for making a TiN barrier for the upper plate of a capacitor to reduce the reactions between the metal oxide and the polysilicon

upper electrode (col. 1, line 26). The TiN layer is formed using $TiCl_4$, which forms chlorine that attacks the metal oxide. The chlorine is reduced by use of an ammonia anneal which chemically attacks the chlorine, and is therefore not a non-reactive ambient.

Applicant respectfully submits that the cited reference of DeBoer does not describe or suggest at least the feature of "... *a metal oxide formed on a surface of a substrate and a CVD high melting point metal nitride film directly formed thereover, wherein said metal nitride film is directly formed on said dielectric film by introducing a source gas containing said high melting point metal into a chamber in which said substrate is contained* ...", as recited in independent claim 1. The cited reference of DeBoer has a polysilicon layer 34 that may be considered to be the substrate as part of the capacitor, but then places a silicon nitride layer 36 over the substrate prior to forming the metal oxide layer 38. Further, the metal nitride layer 40 of DeBoer is not formed on the oxide film by introducing a source gas containing said high melting point metal into a chamber, since the tantalum nitride layer is formed by a reactive nitridation in a nitrogen source such as ammonia. Further, there is no suggestion of a non reactive heat treatment in the cited reference of DeBoer. Independent claim 8 has substantially similar wording and features as claim 1, and independent claim 30 recites "... *forming said titanium nitride (TiN) film on said dielectric film in said CVD film forming device* ...", which is also clearly not suggested by DeBoer since the reference grows the nitride film from reactive conversion of the first tantalum oxide layer, and is not a CVD deposition.

Applicant further respectfully submits that the cited reference of Huang does not describe or suggest at least the feature of "... *a metal oxide formed on a surface of a substrate and a CVD high melting point metal nitride film directly formed thereover, wherein said metal nitride film is directly formed on said dielectric film by introducing a source gas containing said high melting point metal into a chamber in which said substrate is contained* ...", as recited in independent claims 1 and 8. Huang forms a barrier layer between the metal oxide and the substrate to protect the metal oxide. The Huang reference has nothing that comes between the metal oxide and the top electrode 38, and thus clearly can not describe or suggest to anyone the recited step of a CVD high melting point metal nitride film directly formed thereover, wherein said metal nitride film is directly formed on said dielectric film by introducing a source gas containing said high melting point metal. The top metal is formed by sputtering, and therefore can not suggest to anyone the step of introducing a source gas containing the metal, as recited in independent claims 1 and 8. Huang also does not describe or suggest the feature of "... *forming said titanium nitride (TiN) film on said dielectric film in said CVD film forming device* ...", as recited in independent claim 30, since the TiN film is sputtered and is not a CVD operation. In view of the above discussion, applicant respectfully submits that the cited reference of Huang does not provide any suggestion or disclosure to combine with the other cited references to obtain the above noted features of the independent claims, which features are the same ones discussed with respect to DeBoers.

With respect to DeBoer and Huang, it is noted that DeBoer simply shows a capacitor in which tantalum-nitride is formed on a Ta_2SO_5 film and thus the basic

construction of a semiconductor device of DeBoer is completely different from that of the present invention. Similarly, in Huang, the described temperature in nitridation processing is higher than that of the present claimed invention and that therefore it is expected that characteristics of crystals formed thereby as well as the resulting film quality would be significantly different from that of the present claimed invention. Accordingly, it is believed that the technical teaching of these references is very different from that of the present claimed invention and that these references do not appear to show any technical relationship with the present claimed invention. It other words, it is respectfully submitted that, in addition to the other deficiencies of these references set forth herein, these references are not properly combinable to reject the claims of the present application.

Applicant further respectfully submits that the Tamaru reference neither describes nor suggests a non-reactive ambient, but rather teaches using an oxidizing titanium source gas ambient to form a metal layer prior to the introduction of reducing gases such as ammonia, in order to prevent the disassociation of the metal oxide film by a reducing ambient, but rather specifically provides protection from the reactive ambient. Thus the cited reference does not describe or suggest using a non-reactive ambient as recited in the independent claims. Tamaru discloses the use of ammonia to passivate the polysilicon lower electrode, which is not a non-reactive process, but is rather a nitridation process that forms a new material out of the underlying silicon (col. 2, lines 10-24). Tamaru contains no suggestion of the use of ammonia or reducing gas after the dielectric is formed (col. 3, lines 30 -49; col. 4, line 20) until a oxygen containing titanium source gas

has covered the metal oxide with the upper electrode (col. 18, lines 33- 40). The Tamaru reference states that the metal oxide should not come into contact with reducing gases such as ammonia, and thus directly teaches against the recited features of the claimed invention. Applicant respectfully submits that the Tamaru reference teaches using an oxidizing titanium source gas ambient to form a metal layer prior to the introduction of any reducing gas such as ammonia, in order to prevent the disassociation of the metal oxide film by a reducing ambient. Thus the cited reference does not describe or suggest using a non-reactive ambient, nor the feature that when the CVD-TiN film is formed on an oxide metal, the oxide metal is first heated within an NH3 gas or a gas that is non-reactive to the oxide metal. Thereafter, a source gas is supplied to the oxide metal, which grows the TiN film thereon. In this manner, the TiN film is formed directly on the oxide by consuming part of the oxide and converting it. This is not a non reactive process. Since Tamaru discloses forming the protective film on the oxide metal followed by forming the TiN film on the protective layer, then the cited reference of Tamaru does not disclose a process for forming the TiN film or any other metal nitride film directly on the oxide metal, as set forth in Applicant's independent claims 1, 8 and 30. Thus Tamaru does not describe or suggest to one of ordinary skill the missing features of the Huang or DeBoers references.

The Nishikawa reference discloses that using a reaction gas that contains oxygen, which is therefore not a non-reaction ambient with respect to the metal oxide, at up to 5 sccm (col. 5, line 23), and thus produces an oxygen containing metal film, which is the same thing as a film that has been oxidized. Applicant respectfully submits that this is a

process that one of ordinary skill in the art would clearly recognize as not occurring in a non-reactive ambient. Thus the cited reference clearly teaches an ambient that is reactive.

Applicant further respectfully submits that the cited Nishikawa reference teaches an oxidized metal that is not too resistive. Nishikawa teaches using an oxidizing ambient to form a slightly oxidized metal layer, in order to prevent the destruction of the film by a reducing ambient. Oxidizing and reducing a film are both clearly not non-reactive operations. Thus, applicant respectfully submits that the cited reference of Nishikawa teaches using copious amounts of an oxidizing ambient, and thus can not provide the missing features of the DeBoer and Huang references, discussed above.

It is further respectfully submitted that Nishikawa discloses a method for forming a TiN film by flowing oxygen gas and nitrogen gas on to an oxide metal by first reacting with oxygen and then by flowing a gas containing Ti components to the oxide metal. A nitride metal containing oxygen is thus reactively formed as a protection film and successively, after stopping the supply of oxygen, the TiN film is formed. Nishikawa further discloses that a vacuum within a chamber is set at 1.0 Torr when heating, and the vacuum of the chamber is set at 0.15 Torr when the source gas is supplied to the chamber. In contrast, the present claimed invention sets forth that the vacuum in the heating operation, is set at 1 to 0.1 Torr. Applicant notes that in Nishikawa the vacuum level of 0.15 Torr represents the vacuum that is used during a process of forming the Ti film, and the present application shows that such low levels are damaging, as noted in the last two responses. Thus the vacuum levels of the present invention and that disclosed in

Nishikawa are applied to processes that are different with respect to each other. Therefore, Applicant respectfully submits that the TiN film of Nishikawa is formed on a protective film after the protective film containing metal therein has been formed on the dielectric film. Therefore, Applicant respectfully submits that the cited reference of Nishikawa does not disclose a process for forming the TiN film or any other metal nitride film directly on the oxide metal, as set forth in Applicant's independent claims 1, 8 and 30. Thus Nishikawa can not suggest the missing features of the DeBoer and Huang references, discussed above.

In the cited Lee reference, the anneal step occurs after the TiN deposition and not prior to metal deposition as recited in the present invention. Thus the Lee reference is significantly different from the other cited references that teach oxidizing the substrate. Applicant further respectfully submits that the Lee reference discloses an anneal process that occurs after a TiN barrier layer is formed, and thus does not describe or suggest an anneal of the metal oxide, since the barrier is stated to protect the metal oxide. Lee teaches a method of chemically removing residual chlorine gas in a vacuum system. In sum, Lee does not teach protecting the metal oxide film from reducing ambients.

Applicant's independent claim 1 recites utilizing an inert ambient, which is clearly different from any combination of the cited references. Specifically, independent claim 1 recites that "*...metal nitride film is directly formed on said dielectric film by introducing a source gas containing said high melting point metal into a chamber ... said method comprising a step of treating said substrate in an ambient that is non-reactive*

with respect to said metal oxide formed on said surface of said substrate in said chamber wherein said non-reactive ambient includes at least one of a gas non-reactive with respect to said metal oxide contained in said dielectric film and NH_3 gas ...", which is not suggested by any combination of the cited references. Independent claim 8 has very similar wording and features, which for the same reasons given above with respect to claim 1, is neither described nor suggested by any combination of the cited references. Independent claim 30 recites forming said titanium nitride (TiN) film on said dielectric film in said CVD film forming device and in an atmosphere with a gas that is non-reactive with respect to the dielectric film, which is not suggested by any combination of cited references.

Therefore, applicant respectfully submits that independent claims 1, 8 and 30, as amended herein, are not obvious over the suggested combination of cited references, specifically that the suggested combination of references discloses the use of oxidizing or nitridating ambients that are reactive to the underlying metal oxide layers and thus have barriers, in combination with the failure to suggest forming the nitride by CVD with a high melting point metal source gas. Dependent claims 2-7, 9-11 and 13-29, and 31-36 are held to be patentable at least as depending from base claims shown above to patentable over the suggested combination of references. Therefore, for reasons set forth above, applicant respectfully requests that this rejection be reconsidered and withdrawn.

Based on the above, applicant respectfully requests that the Examiner reconsider and withdraw all outstanding rejections and objections. Favorable consideration and allowance are earnestly solicited. Should there be any questions after reviewing this paper, the Examiner is invited to contact the undersigned at 617-951-6676.

Respectfully submitted,
HUTCHINS, WHEELER & DITTMAR

Date: July 12, 2002

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Clean copy of amendments made herein.

1. (Four Times Amended) A method for forming a semiconductor device having a laminated structure including a dielectric film made from a metal oxide formed on a surface of a heated substrate and a CVD high melting point metal nitride film, wherein said metal nitride film is directly formed on said dielectric film by introducing a source gas containing said high melting point metal into a chamber in which said substrate is contained,

said method comprising a step of heating said substrate in an ambient that is non-reactive with respect to said metal oxide formed on said surface of said substrate in said chamber wherein said non-reactive ambient includes at least one of a gas non-reactive with respect to said metal oxide contained in said dielectric film and NH_3 gas, and

introducing into said chamber a source gas for forming said CVD-TiN film and NH_3 gas, following said heating step, and further

wherein a temperature of said substrate is set at a prescribed temperature, before said source gas containing said high melting point metal is introduced into said chamber.

8. (Thrice Amended) A method for forming a semiconductor device having a laminated structure of a dielectric made from a metal oxide and a CVD high melting point metal nitride film formed thereover, wherein said metal nitride film is directly formed on said dielectric film by introducing a source gas containing said high melting point metal into a chamber in which said dielectric film is contained, said method comprising;

heating a substrate onto which said dielectric film is formed to a prescribed temperature in an ambient having a NH_3 atmosphere of no greater partial pressure than 1.0 Torr and no less than 0.1 Torr before the introduction of said source gas containing said high melting point metal.